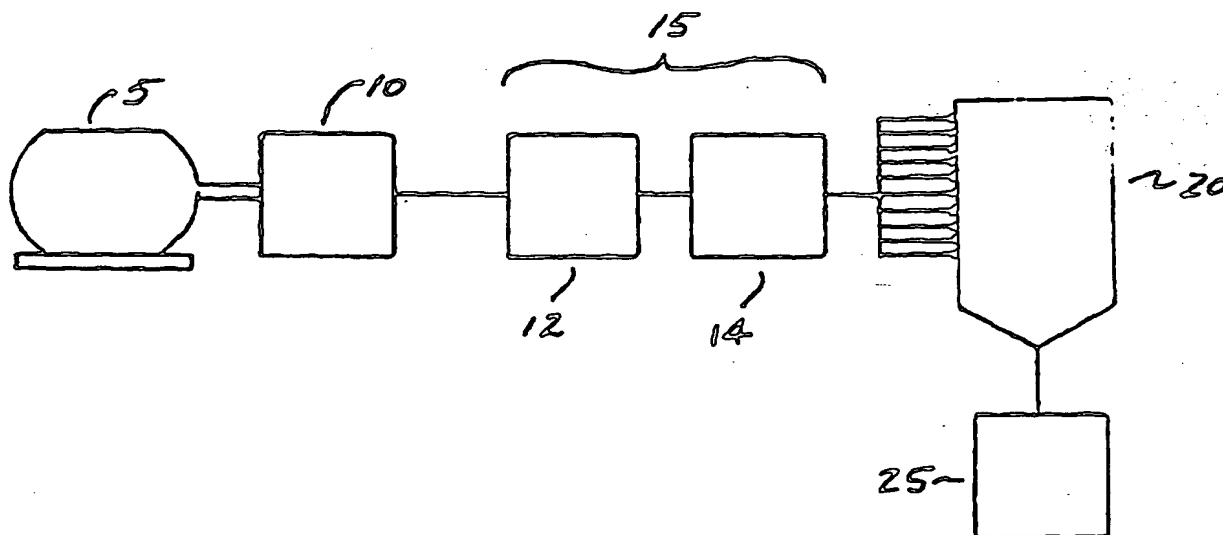




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(54) Title: PULSED ION BEAM ASSISTED DEPOSITION



(57) Abstract

The present invention is for a high-speed, commercial-scale means for deposition of films and coatings on a substrate. The PIBAD (pulsed ion beam assisted deposition) processes [Fig. 4] allow not only deposition, but also special modes of post-deposition treatment of films and coatings, including annealing, melting and regrowth [Fig. 4A], shock wave treatment, and high-pressure plasma redeposition [Fig. 4B] all of which can alter the mechanical, cohesive, and corrosive properties of the final product. In one embodiment of the invention the power system comprises a motor (5) which drives an alternator (10). The alternator delivers a signal to a pulse compression system (15) which has two subsystems, a μ s pulse compressor (12), and a pulse forming line (14). The pulse compression system (15) provides pulses to a linear inductive voltage adder (LIVA) (20) which delivers the pulses to the ion beam source (25).

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Pulsed Ion Beam Assisted Deposition

This application is a Continuation-In-Part of copending U.S. patent application Serial No. 08/340,519, filed November 16, 1994 which is a Continuation-In-Part of U.S. Patent application Serial No. 08/317,948 filed October 4, 1994 which is a Continuation-In-Part of U.S. patent application Serial No. 08/153,248 filed November 16, 1993. This invention was made with Government support under Contract DE-AC04-94AL85000 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

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Background

This invention primarily addresses the general problem of high volume deposition of coating layers for the materials industry. In particular, the current invention solves the problem of low cost, commercial scale deposition of coating materials with properties enhanced beyond those resulting from unassisted deposition techniques.

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A major problem in the general area of physical deposition of one material upon another has been the difficulty of influencing the final state of the overall structure. The primary parameters controlling the results of most physical deposition techniques are the relative heat capacities and thermal conductivities of the substrate material and of the material being deposited. As these material parameters cannot be altered, the most important process control parameter is the substrate temperature, followed closely in importance by the deposition rate.

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The effect of substrate and deposition rate are actually closely related in conventional deposition processes. On an atomic scale, the rate of surface diffusion, which is a thermally activated process, must be high enough that newly deposited atoms are able to find appropriate locations in the structure of the coating before they are trapped in undesirable positions through being covered by additional atoms emitted from the deposition source. It is therefore possible to form

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process control parameter from the substrate temperature T_s and the deposition rate α having the approximate form

$$\beta = \alpha \exp (E / kT_s)$$

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where E is the surface diffusion energy. β is thus the simple ratio between the deposition rate and the rate of surface diffusion steps.

In practice a single simple ratio of this form is not sufficient for prediction of the results of a physical deposition process, primarily because of the existence of competing phases and nonequivalent deposition sites in the growing, but β is often a good first approximation. More important is that a simple quantity such as β , which is determined by the physical and chemical properties of the substrate and the material being deposited, is so nearly predictive of physical deposition processes. This suggests the extremely limited ability of conventional physical deposition control parameters to significantly alter the results of such processes.

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Another important requirement of a physical deposition process is that the deposited layer should adhere adequately to the substrate material. In principle any cohesive force between the two materials would produce some level of adhesion. In practice, however, thermal and mechanical stresses always exist, acting to peel the coating away from the substrate. Even contact pads in microelectronics are subject to small but not insignificant stresses from the bonding wire and from the process of thermocompression bonding used to attach the wire. Accordingly, significant adhesion between the substrate and a coating is usually required for practical applications.

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The considerations listed above and other related problems with physical deposition processes have led to attempts to alter the growth process. Perhaps the most common procedure is to replace a single coating with a multilayer composite coating. This technique is aimed at increasing the adhesion of the top layer to the substrate. In a simple form, one deposits a first layer which exhibits good adhesion to the substrate, then deposits the desired layer on top of the intermediate layer,

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which also exhibits good adhesion to the top layer. The problem with this technique is that adhesion between smooth non-alloyed layers is essentially a function of their surface energy, such that a layer having a low surface energy will adhere strongly to a substrate having a high surface energy. Presumably, then, the reason for poor adhesion is that the desired coating material has higher surface energy than the substrate. (Other reasons will be discussed later.) If so, and an intermediate layer has even lower surface energy than does the substrate, the naive expectation is that the top coating will exhibit even less adhesion to the intermediate layer than to the substrate. This problem most often appears when the interfaces between materials are clean and abrupt.

Given that the surface energy analysis of the use of multilayer coatings to improve adhesion suggests failure of this approach, why are such coatings used? There are many possible reasons for the success of such coatings. A simple example is that introduction of a sufficiently soft layer will allow thermal and mechanical stress to be dissipated as plastic deformation of the soft layer, thereby reducing the stresses acting on the material interfaces. Such an approach has recently been used to allow a submicron GaAs layer to be attached to an Si substrate, a material combination which exhibits large differential thermal expansion stresses.

The main reason for increased adhesion in a multilayer structure is probably that alloying (mixing) of two materials at their mutual interface usually increases adhesion greatly. The reason for this is not entirely clear at this point, but a major contributor is the change in interfacial morphology from a smooth and abrupt planar interface to a fuzzy three-dimensional interface region. In the absence of a clean cleavage plane, stresses across the interface have no natural place to focus, resulting in a much stronger structure. The role of an intermediate layer may thus be that it alloys to some extent with the substrate and the top coating. Such an approach is often rather complicated in actual applications. For example, in microelectronics it is not uncommon to use piles of 4-6 layers of different materials, each requiring a separate deposition process, to form wires and electrodes having adequate adhesion and structural stability.

Part of the difficulty in using the interfacial mixing approach toward increasing adhesion is that such mixing does not occur to the extent desired between most materials under conventional deposition conditions. This is because surface diffusion energies are considerably smaller than bulk diffusion energies. As one generally desires to maximize deposition rate, and hence throughput of the deposition apparatus, the deposition rate is set roughly at a value which allows the atoms being deposited to diffuse about the surface, comfortably finding places in the growing crystal structure before being buried by the next layer. Given that bulk diffusion energies are some 30-100% larger than surface diffusion energies, this implies that in conventional processing there is little if any opportunity for interfacial diffusion to occur. (In fact, a local 'diffusion' of perhaps 2-4 layers in extent will often be seen. This is the result of surface roughening which occurs naturally during growth, and is not due to interfacial diffusion. The interface is still abrupt, but is somewhat irregular rather than flat. This type of mixing does not significantly influence the adhesion between two materials.)

A recent technique for addressing this problem and others (such as avoiding pinholes in films which can destroy the effectiveness of coatings applied as electrical insulators or to improve corrosion resistance) is called Ion Beam Assisted Deposition (IBAD). IBAD is a process currently being researched in which additional vibrational energy is introduced to the near-surface regions of a growing coating through application of a low energy ion beam. The essential idea is that as the kinetic energy of the incoming beam is distributed to atoms in the near-surface region (perhaps the top 3-10 nm) by ion-atom and atom-atom collisions, sufficient energy (~10-20 eV/atom) can be transferred to individual atoms to overcome the kinetic barriers against bulk diffusion. The result is twofold: First, interfacial mixing occurs, and second, the deposited coatings are denser because the ion beam induced bulk diffusion acts to fill in defects in the coating which would lead to pinholes and similar structures. The result is coatings with better adhesion, electronic properties, and corrosion resistance.

Present progress toward developing a practical IBAD process, however, has been limited by the decision to use a continuous ion beam for excitation of the growing coating. This decision seems natural in that the growth process is continuous, and there is no natural time scale (save perhaps for the time required to deposit a single layer of the coating) to suggest the use of a pulsed technique.

There are limitations to the present IBAD approach. Only the near-surface regions (no more than the top few nanometers) are excited by the incident ions. The ion energy is rather low, generally on the order of a few hundred eV. Such an ion, through concatenated collisions, will provide perhaps 50 atoms in a metal with enough energy to overcome local barriers against bulk diffusion before their excitation thermalizes. There are on the order of 10^{16} near-surface atoms per cm^2 of a growth surface. Induction of a single diffusion event for each of these atoms will not greatly influence the final structure. Hence, some presently ill-defined number of excitations per atom will be required to obtain significant improvement in the growing film; experimental results suggest that this number may be on the order of 10 - 100.

The above numbers suggest that the ion dose per cm^2 of surface required to significantly alter the process of physical deposition must be on the order of 10^{15} - 10^{16} ions per cm^2 per layer of atoms deposited. If the dose is much smaller, there will be little or no effect evident on the growing structure. If the dose is much greater, amorphization or other forms of degradation of the excited region is common, owing to the combination of large-scale ion damage of the crystal lattice and the rapid quenching of the damaged regions which prevents regrowth of the crystal. As a result, for a typical growth rate of $\sim 1 \text{ \AA}$ per second, the ion beam current required for IBAD is about 0.1 - 1 milliamp / cm^2 . (This is a relatively high beam current density; accordingly, most experiments to date have actually used lower currents, and hence smaller growth rates.)

The total thermal load on the structure from this level of irradiation is less than 1 watt / cm^2 . As the thermal time constant of the excited region is subnanosecond for many materials, it is clear that there is effectively no local

increase in temperature in the near-surface region. IBAD thus depends solely on nonthermal collision-induced atomic displacements to attain its benefits.

Because IBAD is a nonthermal process, it does not produce alterations in properties of the growing film which depend more upon rapid thermal treatment
5 than on ion beam mixing and densification. Such properties are important for many coating applications, ranging from corrosion-resistant coatings for metals to optical coatings and microelectronics.

For the foregoing reasons, there is a need for a new approach to ion beam assisted deposition which includes a significant transient thermal component as well
10 as the benefits of direct ion-atom collisional effects. A further need is for apparatus capable of carrying out the abovementioned new approach on a commercial scale, said apparatus preferably allowing rapid and economical coating of a wide range of coating/substrate combinations.

Summary

The present invention is directed to a new approach to ion assisted beam deposition, called Pulsed Ion Beam Assisted Deposition (PIBAD), and to apparatus capable of carrying out said new approach, that satisfies the aforementioned needs of the materials industry. The essence of the present invention is the periodic thermal treatment of a thin surface layer (~1-10 μm) during the growth process. Thus, growth and pulsed ion beam are nearly independent processes, the growth process serving primarily to deposit material on a surface, whereupon the pulsed ion beam then converts that material into the desired final structure.

PIBAD thus depends on a fundamentally different approach to material deposition than does the IBAD process. The periodic melting and regrowth (or other transient thermal effects) which occur in the PIBAD process offer the most valuable benefits of the IBAD processes along with profound structural effects not accessible to IBAD. Numerous embodiments and other features, aspects, and advantages of the present invention will become better understood with reference to the following descriptions and appended claims.

Brief Description of the Drawings

The present invention will become more fully understood from the detailed description given herein and the accompanying drawings which are given by way of illustration only, and thus do not limit the present invention. In particular, Figures 1-3 describe an IBEST rapidly repeating pulsed ion accelerator, comprising a Repetitive High Energy Pulsed Power (RHEPP) power source and a Magnetically-confined Anode Plasma (MAP) ion source. However, the detailed description of the IBEST accelerator does not exclude the use of alternate apparatus having similar operating parameters.

10 Figure 1 is a schematic of the RHEPP pulsed power system;

Figure 1A is a circuit diagram of a pulse compression system 15 utilized in the pulsed power system of Figure 1;

Figure 1B is a cross-sectional view of a pulse forming line element;

15 Figure 1C is a cross-sectional view of the Linear Inductive Voltage Adder (LIVA);

Figure 2 is a partial cross-sectional view of the magnetically-controlled anode plasma (MAP) source 25 of the present invention;

Figure 2A is a modified version of Figure 2 showing the magnetic field lines produced by the fast and slow coils in the MAP source'

20 Figure 2B is an expanded view of a portion of Fig. 2 showing the gas inlet valve and the gas inlet channel;

Figure 2C is a schematic diagram of the electric circuit for the fast coil;

Figure 3 is a schematic full cross-sectional view of the MAP ion diode.

25 Figure 4 is a set of schematic diagrams of various aspects of the PIBAD processes.

Figure 4A is a schematic diagram of a process by which material ablated from a first material surface is redeposited onto that surface;

Figure 4B is a schematic diagram of a process by which material ablated from a first material surface is redeposited onto a second material surface; and

30 Figure 4C is a schematic diagram of the treatment of a deposited layer.

Description

The essence of the PIBAD process is to apply a rapidly repeated pulsed thermal treatment of a near-surface region concomitant with the process of growing a material on a substrate, thus altering the characteristic structure of the composite structure. This thermal treatment is applied by irradiating the growth surface with one or more pulses of high current ions during and/or following the growth process. Given a fast enough pulse (~100 nsec for metals), the primary effect of an ion pulse is to dramatically raise the temperature of a thin surface layer, rather than the nonthermal collisional effects associated with ion implantation. Depending on the amount of energy per unit area in the pulse and the depth of penetration of the ions into the composite structure, this thermal energy can be used for three major effects: annealing, melting, or vaporization of the near-surface region of the sample.

Figure 4C illustrates schematically the process of PIBAD treatment of a film 45 grown on a substrate 42. The film is grown by a growth apparatus (not shown). Then the ion pulse generator 40 generates an energetic pulse of ions 41 which intersect the surface of film 45. Depending on the energy and species of the ions, only film 45 may be heated, or both film 45 and substrate 42 may be heated.

Before beginning detailed descriptions of the effects of the pulsed ion beam, however, it is useful to derive approximate relations for some of the physical parameters of interest. This is because the temperature rise and the length of time that a given material is subjected to the temperature rise (i.e., a thermal time constant for the heated layer) vary dramatically between materials. Let σ be the areal energy density of a single ion pulse, λ be the ion penetration depth, κ be the thermal conductivity of the target material, c be the specific heat of the target material, and ρ be the density of the target material. Then the temperature rise associated with absorption of a single ion pulse is approximately

$$\Delta T \sim \sigma / c \rho \lambda,$$

and the thermal time constant for the region heated by the ion pulse is approximately

$$\Delta t \sim c\rho\lambda^2 / \kappa.$$

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Comparison of ΔT and Δt with the material properties of the target and the characteristics of the ion pulse allows one to predict the result of a given PIBAD process.

Ion beam pulses having relatively small amounts of energy can be used to provide a rapid thermal anneal to the composite structure. The ion pulse surface energy densities for the annealing process should be such as to not melt the target, but should come close enough to the melting point (perhaps $0.6-0.99 T_m$) so that the thermal effects are significant during the period in which the target surface remains hot. For example, if a copper target is used, the melting temperature is $\sim 1350^\circ\text{K}$. Beginning at STP, and aiming for a final temperature of $0.9 T_m$, the desired ΔT is $\sim 1100^\circ\text{K}$. If the ion penetration depth λ is $5\text{ }\mu\text{m}$, the first relation above gives the surface energy density of the ion beam pulse as $\sigma \sim 1.9\text{ J/cm}^2$. The thermal time constant of the ion-heated region is $\Delta t \sim 200\text{ nsec}$. For contrast, if the same problem is applied to tungsten, the necessary $\sigma \sim 3.9\text{ J/cm}^2$ and $\Delta t \sim 350\text{ nsec}$. Again, If an indium coating is being put on a copper fitting (for example), σ is only about 0.1 J/cm^2 , while $\Delta t \sim 500\text{ nsec}$. A final metallic example is stainless steel, where the same normalized annealing conditions will require $\sigma \sim 0.6\text{ J/cm}^2$ and the time constant, owing to the lower thermal conductivity of alloys, is $\Delta t \sim 5\text{ }\mu\text{sec}$. Clearly, the desired effect will vary over a wide range of pulse energies depending on what the target material is. As a result, general statements about the amount of energy required and the thermal time constant associated with a given irradiation condition are not possible, but must be calculated roughly for each situation using the above relations.

Another important factor is the rate at which the temperature quenches following the heating effects of the ion pulse. This parameter is approximately $\Delta T/\Delta t \sim \sigma \kappa / (c\rho)^2 \lambda^3$. The quench rate for the above examples range from $\sim 10^{10}$ °K/sec for the copper example to $\sim 10^8$ °K/sec for the stainless steel. Note that the value of $\Delta T/\Delta t$ varies as λ^{-3} , so that the ion penetration depth (or equivalently the ion kinetic energy) is by far the most important parameter in determining the quenching rate.

Somewhat larger amounts of energy deposition will melt the ion penetration depth of the composite structure. The figures above, which still are approximately correct for a melted layer, suggest that in metals the timescale for freezing is on the order of a few hundred nanoseconds, which corresponds to a liquid-solid interface velocity on the order of 10-50 m/sec. Although this motion is very fast, such solid-liquid interfacial velocities in metals are associated with high-quality regrowth of a polycrystalline, or even single crystalline material. The primary application for melting a surface layer is to deposit up to several microns of material between ion pulses, even though at ~ 100 pps this requires a rapid rate of deposition that will produce extremely poor as-deposited material. The ion beam pulse is then used to melt and regrow this material, thereby greatly improving the character of the material. Another application, if the ion pulse penetrates deeply enough that the substrate-growth layer interface is melted, is the formation of a highly alloyed region in many material combinations, even when such alloys are not thermodynamically preferred at the intended operating temperatures for the completed composite structure. Note that, since as much as $10 \mu\text{m}$ of material may be treated by a single ion pulse, and we shall see that the IBEST system is easily capable of pulse rates of 100 pps, in principle the resulting transformation from highly-defective material to high-quality material would make a deposition rate on the order of 1 mm/sec practical. This is a tremendous improvement over conventional physical and/or chemical vapor deposition processes, which more typically deposit $\ll 1 \mu\text{m/sec}$ of high-quality on a surface. The current invention thus has the potential to deposit material at a rate some 3-4 orders of magnitude

faster than existing processes, opening the door to growing machine parts directly by physical deposition, a technique which might be particularly useful for gas turbines and jet engine components.

At still higher ion pulse surface energy densities, the surface layer of the composite structure will be vaporized, again typically to a depth approximating that of the penetration of the ions. This might seem a strange thing to do when the goal is to grow a film. However, there are at least two effects which are potentially useful in growing special structures. First, when a layer is vaporized from a surface, a shock wave is transmitted into the surface. If a 10 μm layer is vaporized in ~ 100 nsec, and the material vaporized has a specific gravity of ~ 10 , the inward propagating shock wave has a magnitude on the order of 1 Gpa, or 10 kbar. Such a shock wave is strong enough to cause plastic flow and dislocation multiplication in almost any materials, thereby dramatically changing the mechanical properties of the non-vaporized remnant surface. In particular, extreme hardening of the surface would be common. Second, when a thin surface layer is turned into high-temperature vapor on a short time scale, it expands toward the surface as well as away from the surface. As a result, some portion of the vaporized material will be redeposited on the surface from whence it came. The resulting surface is likely to have unique properties, as it grows from contact with a low-temperature (~ 1 eV) plasma having a pressure of several thousand atmospheres. Such conditions have never before been accessible in a controllable manner.

This effect is shown schematically in Figure 4A, subfigures 1-4. In subfigure 1, an short pulse of ions 400 approaches the near-surface region 401 of the substrate 402. The thickness of 401 is the ion penetration range in the substrate material, and the total energy of the pulse is sufficient to vaporize the material in 401. In subfigure 2, the pulse of ions has been absorbed by the near-surface region 401, which has now vaporized. However, the pulse is of short enough duration (~ 100 nsec) that the material in 401, although vaporized, has not had time to expand significantly. In subfigure 3, the material in 401 is expanding, although it still has very high pressure and density. Beacuse of the rapid transport of heat away from

the interface between 401 and 402 into the bulk of 402, a layer of redeposited material 403 begins to grow at that interface. Finally, in subfigure 4, all of the vapor made up of the near-surface region has dispersed, and the substrate 402 is coated with a layer of material 403 redeposited from the vapor of 401 during the initial high-temperature and high-pressure stage of the expansion of 401.

Another possibility is that one might desire to vaporize a layer of material thicker than the deposited layer. In such a case, the object would be to alter the properties of the original surface while causing as little evaporation of the original surface as possible. This could be accomplished by depositing a sacrificial layer on the surface, and then applying an ion pulse sufficient to vaporize a surface layer somewhat thicker than the sacrificial layer. If the parameters were carefully chosen, the material redeposited on the surface would be substantially that portion of the original surface which was vaporized. The result is that the surface would have been subjected to a strong shock wave and to a high-pressure high-speed redeposition of the vaporized materials, but would still consist substantially of the original material of the surface, and the location of the final surface would be substantially that of the original surface. The properties of the treated surface, however, would be changed in a manner not accessible even through the rapid melt and regrowth which can be produced using weaker ion beam pulses for thermal treatment.

Another application for the PIBAD process is in the cleaning of volatile materials from surfaces. It is possible to heat a surface sufficiently to remove, for example, a layer of hydrocarbon contaminants without disturbing the underlying structure. Such a cleaning process might be useful in microelectronics, plating, mechanical assembly, and the food industry, removing the problem of using carcinogenic solvents.

The processes outlined are simple illustrations of the potential of the use of pulsed ion beams combined with conventional growth processes. The PIBAD process is primarily controlled by the depth of penetration of the ions and the total energy of the ion pulse. Because there typically are no chemical effects involved in

the use of PIBAD, the identity and kinetic energy of the ions are unimportant as long as the desired penetration depth of the ions is attained. As a result, any accelerator system which can generate pulses of ions having suitable kinetic energy, peak power, and total energy per pulse can be used in the PIBAD processes which make up the present invention. One system in particular, the IBEST system, which is the subject of a copending U.S. patent application (08 /317,948) will be discussed in some detail., but not the invention is not intended to exclude other pulsed ion accelerator systems.

To begin with, the operational parameters of the IBEST system will be outlined. IBEST generally uses ion energies above 20 keV (more generally above 100 keV), and below about 1 MeV, resulting in an ion penetration depth on the order of 1-50 μm , depending on the identity of the ions and the target atoms. This is in sharp contrast to the few nanometers affected in the IBAD process. IBEST apparatus can generate ion energies above 10 MeV, but such energies are not well suited to the present invention. IBEST apparatus appropriate for PIBAD applications typically would have an average power of a hundred kilowatts and a pulse repetition rate of about 100 pps. The total energy per pulse is thus about a kilojoule. Given a pulse duration of some 100 nsec, the peak power of the ion pulse is about 10^{10} watts. As the MAP diode can irradiate an area ranging from about 5-1000 cm^2 , the surface energy density of the ion pulse ranges from about 1-200 J/cm^2 when the IBEST system is operating at full power (100 kW). If lower surface energy densities are required, either the ion beam can be defocused or the energy per pulse can be reduced. There is no fundamental reason that an IBEST system with much larger or smaller capacity cannot be built to fit specific applications. The numbers above are simply to fulfill the need for specificity in considering PIBAD applications, and are not intended to limit the invention in any manner.

The power and timescales described above are sufficient to anneal a coating, melt and regrow a film, or to vaporize a near surface layer. The thermal time constant of the heated layer in metals is about 1-10 times that of the ion pulse itself, so the PIBAD treated material quenches at a rate on the order of 10^8 $^\circ\text{K}/\text{sec}$ or greater, fast enough that the high temperature structure is generally preserved. At

intermediate power levels, the near-surface region melts and then regrows using the underlying atomic structure as a substrate. Such treatment tends to remove undesired structures (e.g., amorphous structures) and to densify the near-surface region. Application of IBEST technology to the problem of material deposition thus provides a previously unknown versatility for controlling the structure of the finished article.

Another important property of the PIBAD approach to film deposition as implemented using the IBEST technology is that a massive increase in the speed of material deposition will often be possible. Consider the case where ion energy and power levels suitable for melt and regrowth of a near-surface region are used. In principle it is only necessary to apply one ion pulse every time an amount of material corresponding to the thickness of the near-surface region is deposited. (In practice a somewhat higher repetition rate may be used, but the assumption will suffice for the present discussion.) It should then be possible to deposit roughly a μm of material or more between ion pulses. Given a pulse repetition rate of 100 pps, the total material deposition rate would be so high that the pre-pulse structure would be highly defective on both the atomic and macro levels. However, the only function of the material deposition process, unlike conventional techniques, is to put material on the growth surface. The material is then altered into the desired structure by the thermal effects of the PIBAD process. This suggests that, using IBEST technology, a high-quality material deposition rate on the order of 0.1 - 1 mm/sec should be possible for materials which can handle the heat load. This rate is 10^4 to 10^6 times faster than any previously known deposition process capable of yielding high-quality structures.

The enormous deposition rate made possible using the PIBAD process makes possible the construction of macroscopic products using physical deposition. An example of such a product would be a gas turbine blade for small natural gas generators. Using the PIBAD process, such a device should take less than 1 hour to grow, using variable aspect deposition masks to define the structure of the turbine blade. The use of multiple PIBAD pulses per growth cycle might make possible

formation of a densified quenched high-temperature structure that might outperform conventional turbine blades.

To take this concept to an extreme, it would be possible in principle to use a PIBAD process to make diesel engines for trucks with a deposition period of a few hours, given an advanced IBEST system capable of irradiating larger areas. The internal and external structures of the engine would be built up using masks, in a manner similar in principle (if not in detail) to the operation of a 3-D laser pantograph. As the alloys could be regrown, heat-treated, shock-treated, and high-pressure vapor redeposited in precise locations, it would not be surprising if a process could be developed to meet the DOT goal of producing a diesel engine for trucks having an expected lifetime of a million miles. The PIBAD system clearly has great potential for manufacture of large-scale commercial products.

There is at least one great problem in the use of PIBAD for manufacture of mechanical components. This is the enormous rate at which a deposition source must deliver the material being deposited to make up the component. If the PIBAD process is implemented using a 100 kW IBEST system, about 1mm/second can be thermally treated over an area of some 100 cm². This means that 10 cm³ of material must be supplied to the growth surface each second. As material is probably going to other surfaces as well, this is a bare minimum rate for the deposition source. No such deposition source exists at this time.

However, the PIBAD process itself can be used as a deposition source. As shown in Figure 4B, a pulsed ion source 40 can irradiate portions of a target material 42 with a sufficiently energetic pulse of ions 41 to vaporize the near surface region of substrate 42, forming a plume 43 of vaporized material. The growth surface 44 can then be positioned so that the plume 43 of vaporized material from the target is captured thereon. Because of the enormous growth rate resulting from this process, a second IBEST system will usually be set up to irradiate the growth surface. This IBEST system will be adjusted to facilitate the PIBAD melt and regrow process, thereby producing high-quality material. It is possible to use a

single IBEST system for irradiation of both the deposition source and the growth surface, but this involves additional beam steering hardware.

How much material is in the vaporization plume? Assume that the ion pulse has a total delivered energy of 10 kJ (thus, a 1 MW IBEST system). Adjust the ion energy and ion identity until a plume having a kinetic energy of about 2 eV results. The vapor then has an effective temperature of about 10000 °K. The total amount of material vaporized is roughly 0.05 gram-mole, or about 3 gms of steel. Some of the material redeposits on the deposition source surface, but how much is a function of the material and the temperature of the plume. However, the amount redeposited will always be much less than half of the total material vaporized. If we assume that half of the vaporized material is lost to redeposition and geometrical factors, then some 1.5 gms of steel, having a volume of $\sim 0.2 \text{ cm}^3$, are delivered to the growth surface per pulse of the 1 MW PIBAD deposition system. At a repetition rate of 100 pps, the total material delivered to the growth surface is $\sim 20 \text{ cm}^3/\text{sec}$, a rate which cannot be matched by any previous deposition system. The rate at which material must be delivered to the growth surface to match the capabilities of a particular pulsed ion beam source used to implement the PIBAD thermal treatment process will depend on the material and geometry of the deposition in ways that are known to one skilled in the art.

The following discussion is a description of the IBEST rapidly repetitive pulsed ion beam system which can be utilized to produce the ion beams for pulsed ion beam assisted deposition. Note, however, that the deposition and thermal treatment processes which are the focus of the present invention do not depend upon any particular ion source, accelerator, or power supply design, so long as the pulsed ion beam output is suitable, as discussed in detail heretofore, for PIBAD processes. For example, pulsed sources of energy for thermal treatment can include lasers, pulses of plasmas, as from plasma railguns, and pulsed electron beams, all of which would be used in a manner similar in essence to the IBEST system.

A variety of ion beam sources exist. Typical ion beam generators use dielectric surface arcing on an anode as a source of ions and thereafter magnetically

or geometrically direct and focus the generated ion beam onto the material of interest. This surface arcing (also called "flashover") destroys the anode surface in less than 100 pulses, and produces a mixed species of ions that cannot be adjusted. Other difficulties arising from flashover include: production of large quantities of neutral gas that makes high repetition rate difficult, generation of debris which can contaminate surfaces being treated, and non-uniformity and irreproducibility of the beam in some cases due to the localized and difficult to control nature of flashover ion sources.

State-of-the-art ion beam generators are typically "one shot" devices, i.e., they operate at low repetition rates ($\ll 1$ Hz). Existing high intensity ion beam generators cannot be operated at high repetition rates ($\gg 1$ Hz) for a number of reasons. First, existing pulsed power supplies are not able to generate electrical pulses at high repetition rates having the voltage, pulse width (i.e., nominal temporal duration), and pulse energy required to generate the ion beams needed for the various beneficial applications described herein. This limitation renders commercial exploitation impractical. However, it should be noted that one shot surface treatments from a robust ion beam source are adequate for some purposes. Second, the design of existing ion beam generators does not allow repetitive operation for an extended number of operating cycles ($\gg 10^3$) without replacement of major components. This limitation would require a maintenance time - manufacturing time ratio incompatible with routine manufacturing operations. Third, existing ion beam generators generally operate with electrical efficiencies $< 5\%$, thus presenting major challenges to the pulsed power supply and the cooling system of the generator. These limitations and others have made it impossible to routinely utilize the conventional ion beam technology described above for pulsed ion beam assisted deposition.

MAP (Magnetically-confined Anode Plasma) ion sources are particularly interesting because of their ability to shield the ion source structure from the destructive effects of the ion plasma by the magnetic shielding created by the magnetic structure of the MAP ion source. However, most of the prior art MAP ion

sources were designed to used in a beam line that also included downstream steering and confinement of the produced ion beams by various electric and/or magnetic fields. This steering and confinement was necessary because of the beam rotation created by the magnetic structure of these MAP ion sources which imparted significant rotation to the produced ion beam. The downstream electric and/or magnetic fields add complexity, size and expense to a system employing such MAP ion sources.

The IBEST system described herein includes a new type of magnetically-confined anode plasma ion beam source. The new MAP ion diode has improvements in a number of areas. Its magnetic fields are designed to have a profile such that the separatrix ($B=0$) between the fast coil field and the slow coil field is located near the anode to minimize or eliminate ion beam rotation. The gas nozzle is designed to produce a high mach number (supersonic) gas flow rate to efficiently localize the gas puff introduced into the ionizing region proximate the fast coil. Means are also provided to create an adjustable bias field to control the formation position of the plasma. A fast ringing field is imposed on the gas puff as it is delivered to the ionizing region to pre-ionize the gas. These and other improvements contribute to making the MAP ion beam source practical for large-scale industrial operations.

The use of the MAP ion diode of this invention for pulsed ion beam assisted deposition processes requires a pulsed high power source. The detailed description below will be devoted to one such source, the Repetitive High Energy Pulsed Power (RHEPP) system developed at Sandia National Laboratories. Other rapidly repeatable pulsed high voltage high power sources could be used as they are developed. For single shot applications other power sources such as Marx generators could also be used.

The MAP ion diode, when combined with the RHEPP source, yields an ion beam generator system capable of high average power and repetitive operation over an extended number of operating cycles for assisting deposition over large surface areas of materials at commercially attractive costs. In particular, the ion beam generator of the present invention can produce high average power (1kW-4MW)

pulsed ion beams at 0.02-20 MeV energies and pulse durations or lengths of from about 10 nanoseconds (ns) - 2 microseconds (μ s), or longer as necessary for the particular application.

The first of the components in the pulsed ion beam generating system is a compact, electrically efficient, repetitively pulsed, magnetically switched, pulsed power system capable of 10^9 pulse operating cycles of the type described by H. C. Harjes, et al, Pro 8th IEEE Int. Pulsed Power Conference (1991), and D. L. Johnson et al., "Results of Initial Testing of the Four Stage RHEPP Accelerator" pp. 437-440 and C. Harjes et al., "Characterization of the RHEPP 1 μ s Magnetic Pulse Compression Module", pp. 787-790, both reprinted in the Digest of Technical Papers of the Ninth IEEE International Pulsed Power Conference, June, 1993, all of which is incorporated by reference herein. These references in conjunction with the discussion herein below place fabrication of such a pulsed power source within the skill of the art.

A block diagram of a power system produced according to the teachings of the present application is shown in Figure 1. From the prime power input, several stages of magnetic pulse compression and voltage addition are used to deliver a pulsed power signal of up to 2.5 MV, 60 ns FWHM, 2.9 kJ pulses at a rate of 120 Hz to an ion beam source for this particular system. The power system converts AC power from the local power grid into a form that can be used by an ion beam source.

Referring to Figure 1, in one embodiment of the invention, the power system comprises a motor 5 which drives an alternator 10. The alternator 10 delivers a signal to a pulse compression system 15 which has two subsystems, a 1 μ s pulse compressor 12 and a pulse forming line 14. The pulse compression system 15 provides pulses to a linear inductive voltage adder (LIVA) 20 which delivers the pulses to the ion beam source 25.

The alternator 10 according to one embodiment is a 600 kW, 120 Hz alternator. In the unipolar mode, it provides 210 A rms at a voltage of 3200 V rms with a power factor of 0.88 to the magnetic switch pulse compressor system 15. The

alternator is driven by a motor connected to the local 480V power grid. The particular alternator used herein was designed by Westinghouse Corporation and fabricated at the Sandia National Laboratories in Albuquerque, New Mexico. It is described in detail in a paper by R. M. Calfo et al., "Design and Test of a Continuous
5 Duty Pulsed AC Generator" in the Proceedings of the 8th IEEE Pulsed Power Conference, pp. 715-718, June, 1991, San Diego, California. This reference is incorporated herein in its entirety. This particular power system was selected and built because of its relative ease in adaptability to a variety of loads. Other power sources may be used and may indeed be better optimized to this particular use. For
10 example, a power supply of the type available for Magna-Amp, Inc. comprising a series of step-up transformers connected to the local power grid feeding through a suitably-sized rectifier could be used. The present system however has been built and performs reasonably well.

In one embodiment, the pulse compression system 15 is separated into two subsystems, one of which is a common magnetic pulse compressor 12 composed of a plurality of stages of magnetic switches (i.e., saturable reactors) the operation of which is well known to those skilled in the art. This subsystem is shown in more detail in Fig. 1A. The basic operation of each of the stages is to compress the time width (transfer time) of and to increase the amplitude of the voltage pulse received
20 from the proceeding stage. Since these are very low loss switches, relatively little of the power is wasted as heat, and the energy in each pulse decreases relatively little as it moves from stage to stage. The specific subsystem used herein is described in detail by H. C. Harjes, et al., "Characterization of the RHEPP 1 μ s Magnetic Pulse Compression Module", 9th IEEE International Pulsed Power Conference, pp. 787-
25 790, Albuquerque, NM, June, 1993. This paper is incorporated by reference herein in its entirety. These stages as developed for this system are physically quite large. In the interest of conserving space, it would be possible to replace the first few stages with appropriately designed silicon control rectifiers (SCR's) to accomplish the same pulse compression result.

These stages 12 convert the output of the alternator 10 into a 1 μ s wide LC charge waveform which is then delivered to a second subsystem 14 comprising a pulse forming line (PFL) element set up in a voltage doubling Blumlein configuration. The PFL is a triaxial water insulated line that converts the input LC charge waveform to a flat-top trapezoidal pulse with a design 15 ns rise/fall time and a 60 ns FWHM. The construction and operation of this element is described in detail by D. L. Johnson et al. "Results of Initial Testing of the Four Stage RHEPP Accelerator", 9th IEEE International Pulsed Power Conference, pp.437-440, Albuquerque, NM, June, 1993. This paper is also incorporated by reference in its entirety. A cross sectional view of the PFL is shown in Figure 1B.

The pulse compression system 15 can provide unipolar, 250 kV, 15 ns rise time, 60 ns full width half maximum (FWHM), 4 kJ pulses, at a rate of 120 Hz, to the linear inductive voltage adder (LIVA) (20). In a preferred embodiment, the pulse compression system 15 should desirably have an efficiency >80% and be composed of high reliability components with very long lifetimes ($\sim 10^9$ - 10^{10} pulses). Magnetic switches are preferably used in all of the pulse compression stages, MS1-MS5, because they can handle very high peak powers (i.e., high voltages and currents), and because they are basically solid state devices with a long service life. The five compression stages used in this embodiment as well as the PFL 14 are shown in Fig. 1A. The power is supplied to the pulse compression system 15 from the alternator 10 and is passed through the magnetic switches, MS1-MS5, to the PFL 14. The PFL is connected to the linear induction voltage adder (LIVA) 20 described below. The second and third magnetic switches, MS2 and MS3, are separated by a step-up transformer T1 as shown. Switch MS6 is an inversion switch for the PFL.

The pulse forming line (PFL) element 14 is shown in schematically in Fig. 1A and in cross section in Fig. 1B. MS6 in Fig. 1A corresponds to the inversion switch 302 shown in Fig. 1B located on the input side of the tri-axial section 314 of the PFL. Output switches 304 and charging cores 306 are also shown. The regions 310 are filled with deionized water as the dielectric. The interior region 308 is filled with air and oil coiling lines, not shown, for the output switches 304. The output of the PFL

is fed in parallel to each of the individual LIVA stages 20, with the positive component flowing through conductors 316 and the shell 318 of the PFL serving as ground. The positive conductors 316 are connected to each of the LIVA stages.

The LIVA (20) is preferably liquid dielectric insulated. It is connected to the output of the PFL and can be configured in different numbers of stages to achieve the desired voltage for delivery to the ion beam source. The LIVA 20 can deliver nominal 2.5 MV, 2.9 kJ, pulses at a rate of 120 Hz to the ion beam source 25 when configured with 10 stages of 250 kV each. For most of the ion beam treatments, the LIVA was configured with four stages of 250 kV each, such that the LIVA delivered a total of 1.0 MV to the ion beam source. However, this voltage can be increased or decreased by changing the number of stages in the LIVA to match the particular material processing need. The nominal output pulse of the LIVA 20 is the same as that provided to it by the PFL, namely, trapezoidal with 15 ns rise and fall times and 60 ns FWHM (full width half maximum). Figure 1C shows a cross section of the four stage LIVA. The four stages, 320, 322, 324, and 326, are stacked as shown and fed the positive pulses from the PFL via the cables 321, 323, 325, and 327. The stages are separated by gaps 330 and surrounded by transformer oil for cooling. The output from each of the LIVA stages adds to deliver a single total pulse to the ion beam source shown here schematically as 25 which is located within a vacuum chamber 332, shown in partial view. As with the PFL, the outside shell of the LIVA is connected to ground.

The power system P (Figure 1) as described, can operate continuously at a pulse repetition rate of 120 Hz delivering up to 2.5 kJ of energy per pulse in 60 ns pulses. The specific power system described here can deliver pulsed power signals of about 20-1000 ns duration with ion beam energies of 0.25-2.5 MeV. The power system can operate at 50% electrical efficiency from the wall plug to energy delivered to a matched load. The power system P uses low loss pulse compression stages incorporating, for example, low loss magnetic material and solid state components, to convert AC power to short, high voltage pulses.

The ability to produce voltages from 250 kV to 20 MV by stacking voltage using a plurality of inductive adders incorporating low loss magnetic material is a principle feature when high voltages are needed, although it is also possible to use a single stage pulse supply, eliminating the need for the adder.

5 The power system can operate at relatively low impedances ($< 100\Omega$) which sets it apart from many other repetitive, power supply technologies, such as transformer-based systems. This feature allows large pulse currents to be attained at reasonable voltages, enabling high treatment rates and the treatment of large areas (5 to more than 1000 cm^2) with a single pulse so as to reduce edge effects
10 occurring at the transition between treated and untreated areas.

The second component of the pulsed ion beam system is the MAP ion beam source 25, shown in Figure 2. The MAP ion beam source is capable of operating repetitively and efficiently to utilize the pulsed power signal from the power system efficiently to turn gas phase molecules into a high energy pulsed ion beam. It can
15 also be operated in the single shot mode, as necessary for a particular application. A precursor of the ion beam source is an ion diode described generally by J. B. Greenly et al, "Plasma Anode Ion Diode Research at Cornell: Repetitive Pulse and 0.1 TW Single Pulse Experiments", Proceedings of 8th Intl. Conf. on High Power Particle Beams (1990) all of which is incorporated by reference herein. Although
20 this reference ion diode differs significantly from the ion diode utilized in the present system as discussed above, the background discussion in this reference is of interest.

The ion beam source 25 is shown in Figure 2. The ion beam source 25 is a magnetically-confined anode plasma (MAP) source. Figure 2 is a partial cross-sectional view of one symmetric side of the ion beam or MAP source 25. The ion
25 beam or MAP source 25 produces an annular ion beam K which can be brought to a broad focus symmetric about the axis X-X 400 shown. In the cathode electrode assembly 30 slow (1ms rise time) magnetic field coils 414 produce magnetic flux S (as shown in Fig. 2A) which provides the magnetic insulation of the accelerating gap between the cathodes 412 and the anodes 410. The anode electrodes 410 also act as
30 magnetic flux shapers. The slow coils 414 are cooled by adjacent water lines, not

shown, incorporated into the structure 30 supporting the cathodes 412 and the slow coils 414. The main portion of the MAP structure shown in this Figure is about 18 cm high and wide. The complete MAP ion diode can be visualized as the revolution of the cross-sectional detail of Fig. 2 about the central axis 400 of the device to form a cylindrical apparatus. A full cross sectional view appears in Fig. 3.

The ion beam or MAP source 25 operates in the following fashion: a fast gas valve assembly 404 located in the anode assembly 35 produces a rapid (200 μ s) gas puff which is delivered through a supersonic nozzle 406 to produce a highly localized volume of gas directly in front of the surface of a fast driving coil 408 located in an insulating structure 420. The nozzle is designed to prevent any transverse flow of non-ionized gas into the gap between the anodes 410 and cathodes 412. After pre-ionizing the gas with a 1 ms induced electric field, the fast driving coil 408 is fully energized from the fast capacitor 150, inducing a loop voltage of 20 kV on the gas volume, driving a breakdown to full ionization, and moving the resulting plasma toward the anode electrodes 410 in about 1.5 μ s or less, to form a thin magnetically-confined plasma layer. The plasma momentarily stagnates at this $B=0$ region, the separatrix, next to the insulating field S produced by the slow coils 414, awaiting the delivery of the main accelerating positive electrical pulse to be delivered at the anodes 410 from the LIVA discussed above.

The pre-ionization step is a departure from the earlier MAP reference which showed a separate conductor located on the face of a surface corresponding to the insulating structure 420 herein. Since this conductor was exposed to the plasma, it broke down frequently. It was discovered that the separate pre-ionizing structure was unnecessary. The gas can be effectively pre-ionized by placing a small ringing capacitor 160 in parallel with the fast coil. The field oscillations produced by this ringing circuit pre-ionize the gas in front of the anode fast coil. A schematic electrical diagram of this circuit is shown in Fig. 2C.

It has also been demonstrated that, prior to provision of the main pulse to the fast coil, it is beneficial to have the ability to adjust the configuration of the magnetic field in the gap between the fast coil and the anode to adjust the initial position of

plasma formation in the puffed gas pulse prior to the pre-ionization step. This is accomplished by the provision of a slow bias capacitor 180 and a protection circuit both being installed in parallel with the fast coil and isolated therefrom by a controllable switch S2. A slow bias field is thus created prior to pre-ionization of the gas by the fast coil. This circuit is also shown in Fig. 2C.

In further explanation of the electrical circuit for the fast coil as shown in Fig. 2C, the bias field capacitor 180 drives a greater than 1 microsecond risetime current in the fast coil before the main capacitor pulse begins. This allows adjustment of the field configuration produced by the fast capacitor current. The fast capacitor 150 drives a 1 microsecond risetime pulse in the fast coil. The preionizer capacitor 160 causes the voltage across the fast coil to ring with a much less than 1 microsecond period, inducing a large oscillating electric field in the gas to be ionized, leading to partial ionization of the gas. The rising magnetic field produced by the fast coil 408 pushes the ionized gas away from the fast coil, stagnating it against the preexisting magnetic field from the slow coil 414.

After pre-ionization the fast coil is then fully energized as described above to completely breakdown the gas into the plasma. After this pulse the field collapses back into the fast coil which is connected to a resistive load which is in turn connected to a heat sink, not shown. In the present embodiment, cooling channels in the supporting structure are used, but other solutions are possible and relatively straightforward. In this manner heat build up in the fast coil is avoided.

The fast coils 408 have been redesigned from the reference fast coils in several ways as well as the heat sinking mentioned above. The gap between the fast coil and the anode electrodes 410 has been reduced with the result that the amount of necessary magnetic energy has been decreased by over 50%. The lower energy requirement permits repetitive use at higher frequencies and reduces the complexity of the feed system voltages for the fast coils. The design of the flux-shaping anode electrode assembly has also contributed to these beneficial results.

The pulsed power signal from the power system is then applied to the anode assembly 35, accelerating ions from the plasma to form an ion beam K. The slow (S)

and fast (F) magnetic flux structures, at the time of ion beam extraction, are shown in Figure 2A. The definite separation between the flux from the fast coil from the flux from the slow coil is shown therein. This is accomplished by the flux-shaping effects of the anodes 410 and also by the absence of a slow coil located in the insulating structure 420 as was taught in the earlier MAP reference paper. The slow coils in the present MAP ion diode are located only in the cathode area of the MAP. This anode flux shaping in conjunction with the location of slow coils in the cathode assembly is different from that shown in the MAP reference paper and permits the high repetition rate, sustained operation of the MAP diode disclosed herein. This design allows the $B=0$ point (the separatrix) to be positioned near the anode surface, resulting in an extracted ion beam with minimal or no rotation. This minimal rotation is necessary for effective delivery of the beam to the material to be treated.

Figure 2B is a detailed view of the gas valve assembly 404 and the passage 425 which conducts the gas from the valve 404 to the area in front of the fast coil 408. The passage 425 has been carefully designed to deposit the gas in the localized area of the fast coil with a minimum of blow-by past this region. The details of the cross sections of the passage 425 were designed for supersonic transport of the gas puff. The design was done with readily available gas flow computer programs and is within the skill in the art. The gas valve flapper 426 is operated by a small magnetic coil 428 which opens and closes the flapper 426 upon actuation from the MAP control system. The flapper valve is pivoted on the bottom end 427 of the flapper. The coil 428 is mounted in a high thermal conductivity ceramic support structure 429 which is in turn heat sunk to other structure, not shown. Alternatively, externally cooled wires surrounding the coil could also serve to extract the heat from the coils. This heat sinking is necessary for the sustained operating capability of the MAP. The gas is delivered to the valve from a plenum 431 behind the base of the flapper. The plenum 431 should be visualized as being connected to a larger plenum located at the central core of the complete MAP ion diode as shown in Fig. 3.

The vacuum in the nozzle 406 rapidly draws the gas into the MAP once the flapper 426 is opened. The function of the nozzle is to produce a directed flow of gas only in the direction of flow and not transverse to it. Such transverse flow would direct gas into the gap between the anode and the cathode which would produce detrimental arcing and other effects. The reduction of the fast coil-anode gap discussed above makes the design of the nozzle very important to the successful operation of the MAP. Fortunately, gas flow design tools are available and were used to develop a nozzle with improved gas flow (higher mach number) and minimal boundary effects. This improved nozzle has an enlarged opening into the gap between the fast coil and the near edge of the anode which tapers from 9 to 15 mm instead of the straight walled 6 mm conduit in the reference MAP. The operating pressure of the gas in the puff valve has been increased from the range of 5-25 psig to the range of 25-40 psig. Experiments have confirmed much improved MAP operation as a result of this new design.

The MAP ion diode described above is distinguished from prior art ion diodes in several ways. Due to its low gas load per pulse, the rate of vacuum recovery within the MAP allows sustained operation up to and above 100 Hz. As discussed above, the magnetic geometry is fundamentally different from previous ion diodes. Prior diodes produced rotating beams that were intended for applications in which the ion beam propagates in a strong axial magnetic field after being generated in the diode. The present system requires that the ion beam be extracted from the diode to propagate in field-free space a minimum distance of 20-30 cm to a material surface. The magnetic configurations of previous ion diodes are incapable of this type of operation because those ion beams were forced by the geometries of those diodes to cross net magnetic flux and thus rotate. Such beams would rapidly disperse and be useless for the present purposes. Moving the slow coils (the diode insulating magnetic field coils) to the cathode side of the diode gap eliminated the magnetic field crossing for the beam but required a total redesign of the magnetic system for the anode plasma source.

The modifications to the fast coil discussed above result in energy efficiency 5-10 times greater than exhibited in previous configurations. The modifications include: the elimination of a slow coil on the anode side of the diode and its associated feeds, better control over the magnetic field shaping and contact of the anode plasma to the anode electrode structure through use of the partially field-penetrable electrodes, the elimination of the separate pre-ionizer coil from the prior ion diodes, the circuit associated with the fast coil to provide "bias" current to adjust the magnetic field to place the anode plasma surface on the correct flux surface to eliminate beam rotation and allow optimal propagation and focusing of the beam, and the redesign of the gas nozzle to better localize the gas puff which enables the fast coil to be located close to the diode gap which in turn reduces the energy requirements and complexity of the fast coil driver.

The plasma can be formed using a variety of gas phase molecules. The system can use any gas (including hydrogen, helium, oxygen, nitrogen, fluorine, neon, chlorine and argon) or vaporizable liquid or metal (including lithium, beryllium, boron, carbon, sodium, magnesium, aluminium, silicon, phosphorous, sulfur, and potassium) to produce a pure source of ions without consuming or damaging any component other than the gas supplied to the source. As described, the ions will be singly ionized in the accelerator, but the MAP diode can be redesigned to supply more power in the ionization cycle to produce multiply ionized ions, thus giving higher ion energies for a given accelerating voltage. The ion beam propagates 20-30 cm in vacuum ($\sim 10^{-3}$) to a broad focal area (5 - 1000 cm²) at the target plane 195, shown in Fig. 3, where material samples are placed for treatment.

The ion beam or MAP source 25 is capable of operating at repetitive pulse rates of 100 Hz continuously with long component lifetimes $>10^6$. The ion beam or MAP source 25, according to the principles of the present invention, draws ions from a plasma anode rather than a solid dielectric surface flashtube anode used in present single pulse ion beam sources. One therefore has precise control over the components in the ion beam by control of the composition of the gas source.

The MAP ion diode and the RHEPP source are the essential components of the IBEST pulsed ion beam generator system. Such a system is capable of high average power and repetitive operation over an extended number of operating cycles for assisting deposition over large surface areas of materials at commercially
5 attractive costs.

The description of the present invention, methods, apparatus, and products of transmutation of atomic nuclei, has been presented in terms of an IBEST ion beam generator system. However, the present invention need not be based on this system, and is intended to be limited only by the description of the physical requirements for
10 the present invention and by the claims appended to this description.

Claims

1. A method for pulsed ion beam assisted deposition of a material on a substrate, comprising:

- 5 a) deposition of said material on the substrate, producing thereby a composite structure; and
b) thermal treatment of the composite structure through the action of at least one ion beam pulse.

10 2. The method of Claim 1, wherein the rate of deposition of said material is continuous in time.

3. The method of Claim 1, wherein the rate of deposition is discontinuous in time.

15 4. The method of Claim 1, wherein said thermal treatment of the composite structure comprises melting and regrowth of a thin surface layer.

5. The method of Claim 1, wherein said thermal treatment of the composite structure comprises annealing without melting of a thin surface layer.

20 6. The method of Claim 1, wherein said thermal treatment of the composite structure comprises vaporization of a thin surface layer.

25 7. The method of Claim 4, wherein the thickness of the thin surface layer subjected to melting and regrowth is greater than the thickness of material deposited.

8. The method of Claim 7, wherein alloying of the material deposited and the substrate material takes place.

The method of Claim 4, wherein the thickness of the thin surface layer subjected to melting and regrowth is less than the thickness of material deposited.

10. The method of Claim 4, wherein the thickness of the thin surface layer
5 subjected to melting and regrowth is substantially equal to the thickness of material deposited.

11. The method of Claim 4, wherein multiple ion beam pulses are applied to the
10 composite structure.

12. The method of Claim 12, wherein the thickness of the thin surface layer
subjected to melting and regrowth is greater than the thickness of material deposited
since application of the previous ion beam pulse.

13. The method of Claim 12, wherein said melting and regrowth produces high-
15 quality deposited material.

14. The method of Claim 11, wherein the thickness of the thin surface layer
subjected to melting and regrowth is less than the thickness of material deposited
20 since application of the previous ion beam pulse.

15. The method of Claim 11, wherein the thickness of the thin surface layer
subjected to melting and regrowth is substantially equal to the thickness of material
deposited since application of the previous ion beam pulse.

25 16. The method of Claim 5, wherein said annealing without melting allows
recovery of a high-temperature phase in the composite structure.

17. The method of Claim 5, wherein said annealing without melting allows
30 recovery of a nonequilibrium phase in the composite structure.

18. The method of Claim 5, wherein the thickness of the thin surface layer subjected to annealing without melting is greater than the thickness of material deposited.

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19. The method of Claim 5, wherein the thickness of the thin surface layer subjected to annealing without melting is less than the thickness of material deposited.

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20. The method of Claim 5, wherein the thickness of the thin surface layer subjected to annealing without melting is substantially equal to the thickness of material deposited.

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21. The method of Claim 5, wherein multiple ion beam pulses are applied to the composite structure.

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22. The method of Claim 21, wherein the thickness of the thin surface layer subjected to annealing is greater than the thickness of material deposited since application of the previous ion beam pulse.

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23. The method of Claim 21, wherein the thickness of the thin surface layer subjected to annealing without melting is substantially equal to the thickness of material deposited since application of the previous ion beam pulse.

24. The method of Claim 21, wherein the thickness of the thin surface layer subjected to annealing without melting is substantially equal to the thickness of material deposited since application of the previous ion pulse.

30

25. The method of Claim 6, wherein said vaporization of a thin surface layer sends a shock wave into the bulk of the composite structure.

26. The method of Claim 6, wherein said vaporization of a thin surface layer produces a dense, high-pressure plasma cloud, part of which redeposits on the composite structure.

5

27. The method of Claim 6, wherein the thickness of the thin surface layer subjected to vaporization is greater than the thickness of material deposited.

10

28. The method of Claim 6, wherein the thickness of the thin surface layer subjected to vaporization is less than the thickness of material deposited.

29. The method of Claim 6, wherein the thin surface layer is composed of contaminants, and the amount of material vaporized is adjusted to remove the thin surface layer while producing minimal change of the underlying structure.

15

30. The method of Claim 6, wherein multiple ion beam pulses are applied to the composite structure.

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31. The method of Claim 30, wherein the thickness of the thin surface layer subjected to vaporization is greater than the thickness of material deposited since application of the previous ion beam pulse.

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32. The method of Claim 30, wherein the thickness of the thin surface layer subjected to vaporization is less than the thickness of material deposited since application of the previous ion beam pulse.

30

33. The method of Claim 30, wherein the thickness of the thin surface layer subjected to vaporization is substantially equal to the thickness of material deposited since application of the previous ion beam pulse.

34. A method for rapid vaporization of large quantities of a target material, comprising irradiating a thin surface layer of said target material with a rapidly repetitive pulsed ion beam.

5 35. A method for vapor-phase manufacture of mechanical components, comprising:

- a) means for rapid growth of material upon a substrate;
- b) time-variable means for masking off regions of the substrate from the growth process; and
- 10 c) means for thermally treating said material.

36. The method of Claim 35, further comprising time-variable means for masking off regions of the material from said means for thermal treatment.

15 37. The method of Claim 35, wherein said means for thermally treating said material comprises use of a pulsed ion beam source.

38. The method of Claim 35, wherein said means for rapid growth upon a substrate comprises vaporization of a target, said target comprising said material, through the action of a pulsed ion beam source.

20 39. An apparatus for pulsed ion beam assisted deposition, comprising:

- a) a substrate;
- b) a deposition source which deposits a material on said substrate, thereby forming a composite structure; and
- 25 c) a pulsed ion beam source which irradiates said composite structure.

40. The apparatus of Claim 39, wherein said deposition source deposits a material on said substrate at a non-zero rate until the deposition process is completed.

30

41. The apparatus of Claim 39, wherein said deposition source deposits a material on said substrate in discrete pulses until the deposition process is completed.

5

42. The apparatus of Claim 39, wherein the pulsed ion beam source irradiates only the material deposited on the substrate.

43. The apparatus of Claim 39, wherein the pulsed ion beam source irradiates both the material deposited on the substrate and a thin surface layer of the substrate.

10

44. The apparatus of Claim 39, wherein the pulsed ion beam source irradiates said composite structure with multiple ion beam pulses during the deposition of material on the substrate.

15

45. The apparatus of Claim 44, wherein the ion beam pulses vaporize a thin surface layer of the growing composite structure.

46. The apparatus of Claim 44, wherein the ion beam pulses vaporize a thin surface layer of the growing composite structure.

20

47. The apparatus of Claim 44, wherein the ion beam pulses anneal a thin surface layer of the growing composite structure.

25

48. The apparatus of Claim 41, wherein said deposition source comprises a pulsed source of energy incident on a target comprising the material to be deposited, the energy of the ion beam pulses incident on said body providing sufficient energy to convert a thin surface layer of said target to vapor, the overall geometry of the

system being such that a substantial portion of said vapor is projected toward and deposits on the substrate.

49. The apparatus of Claim 48, wherein said pulsed source of energy comprises a
5 deposition pulsed ion beam source.

50. The apparatus of Claim 49, wherein said deposition pulsed ion beam source
and said pulsed ion beam source share components.

10 51. The apparatus of Claim 48, wherein said pulsed source of energy comprises a
pulsed laser.

52. The apparatus of Claim 48, wherein said pulsed source of energy comprises a
plasma discharge.

15

53. The apparatus of Claim 39, further comprising time-variable means for
masking off regions of the substrate from said deposition source.

54. The apparatus of Claim 39, further comprising time-variable means for
20 masking off regions of the composite structure from said pulsed ion beam source.

55. The apparatus of Claim 48, wherein said pulsed source of energy comprises a
pulsed electron beam.

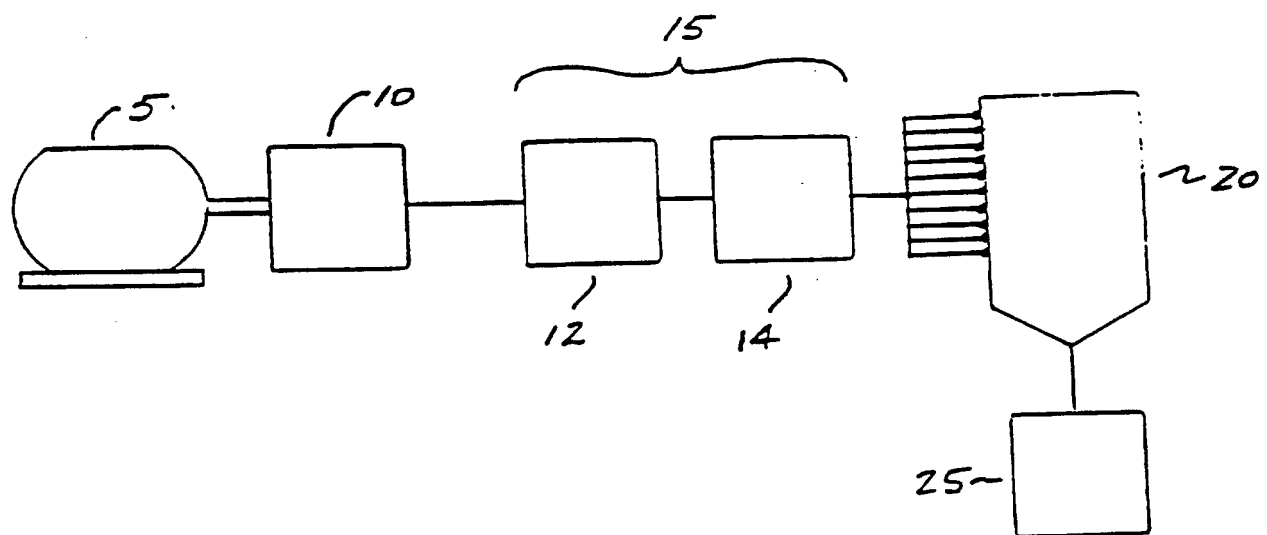


FIG. 1

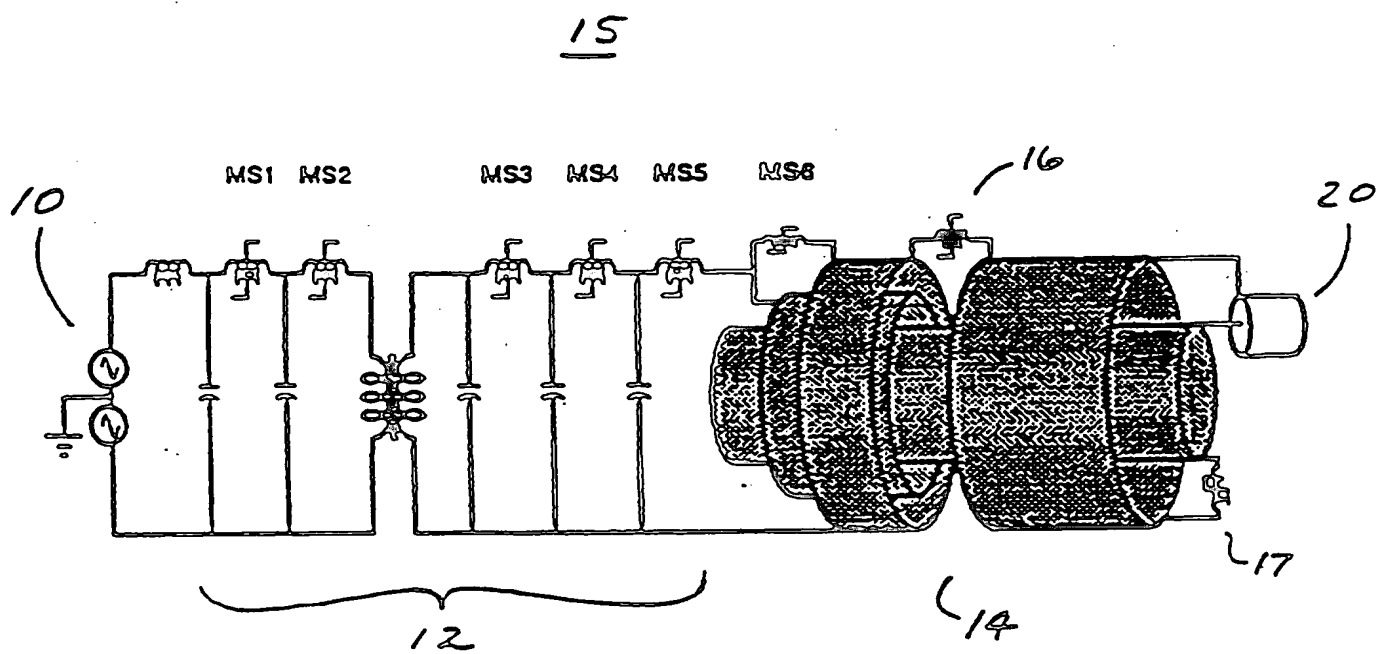


FIG. 1A

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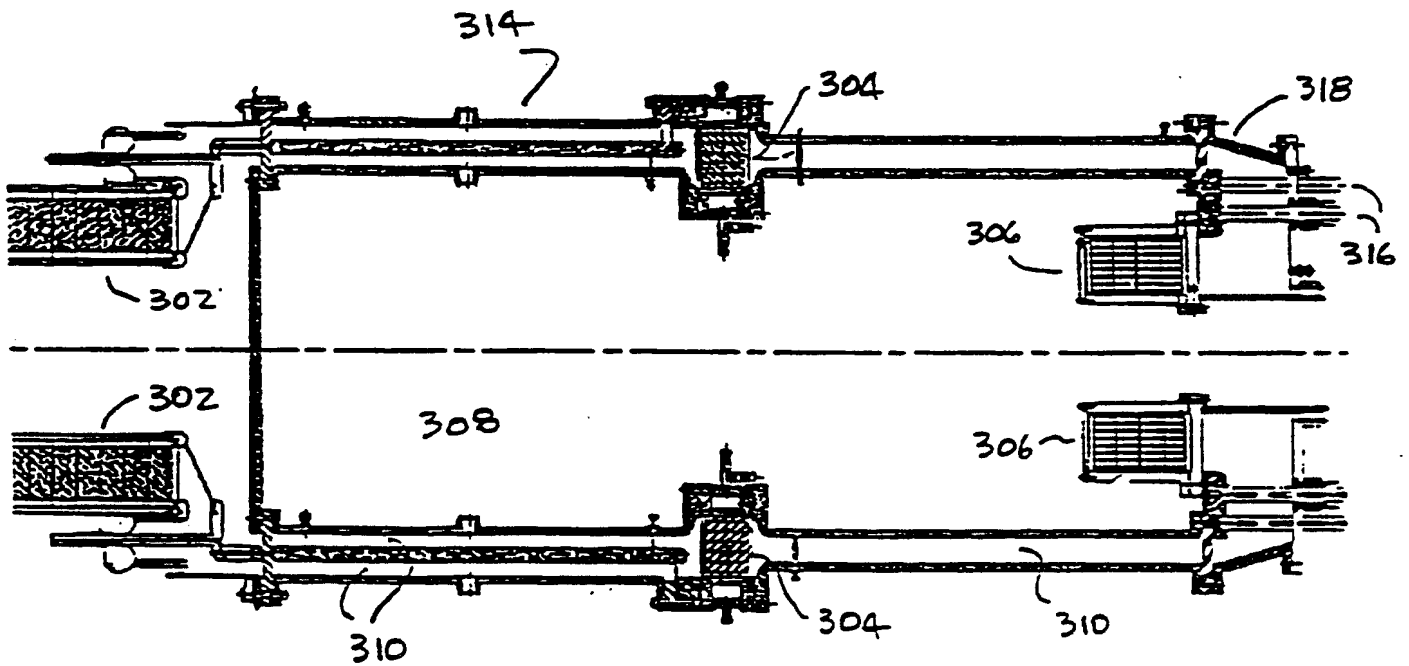


FIG. 1B

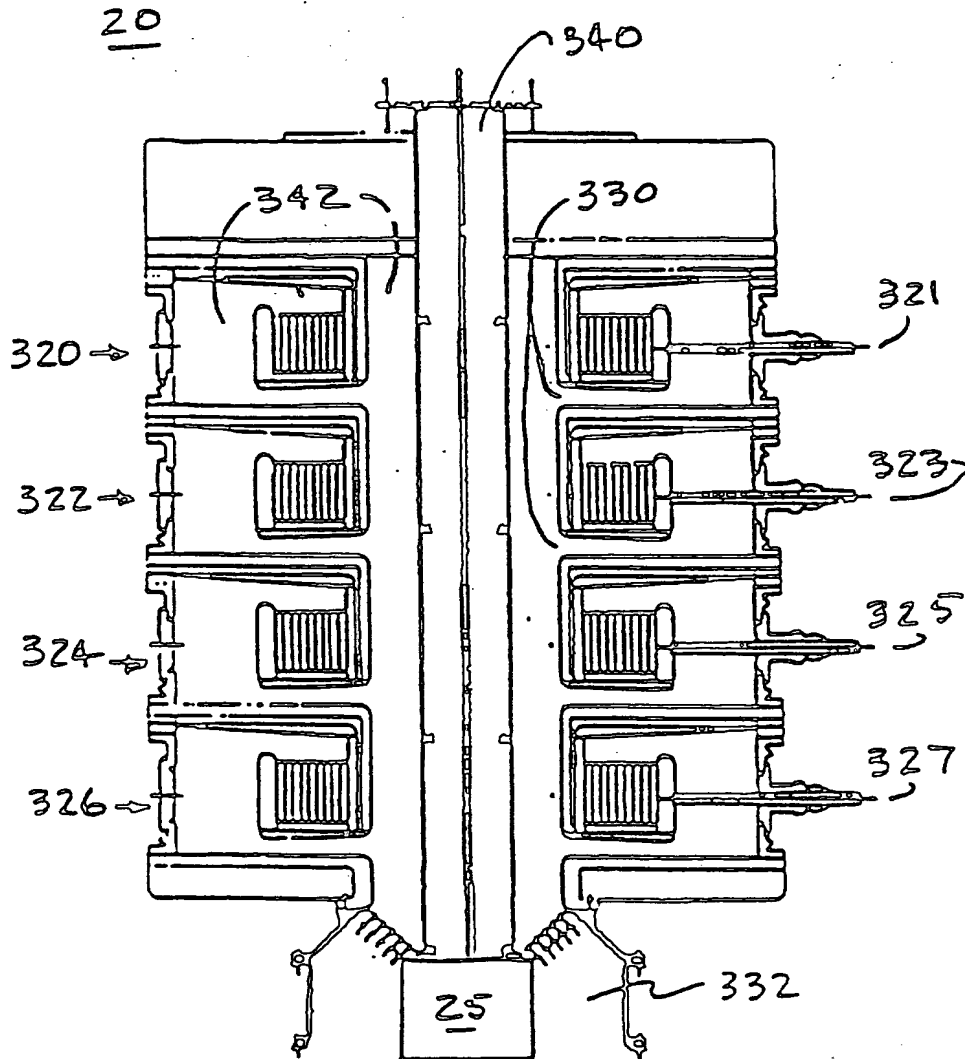


FIG. 1C

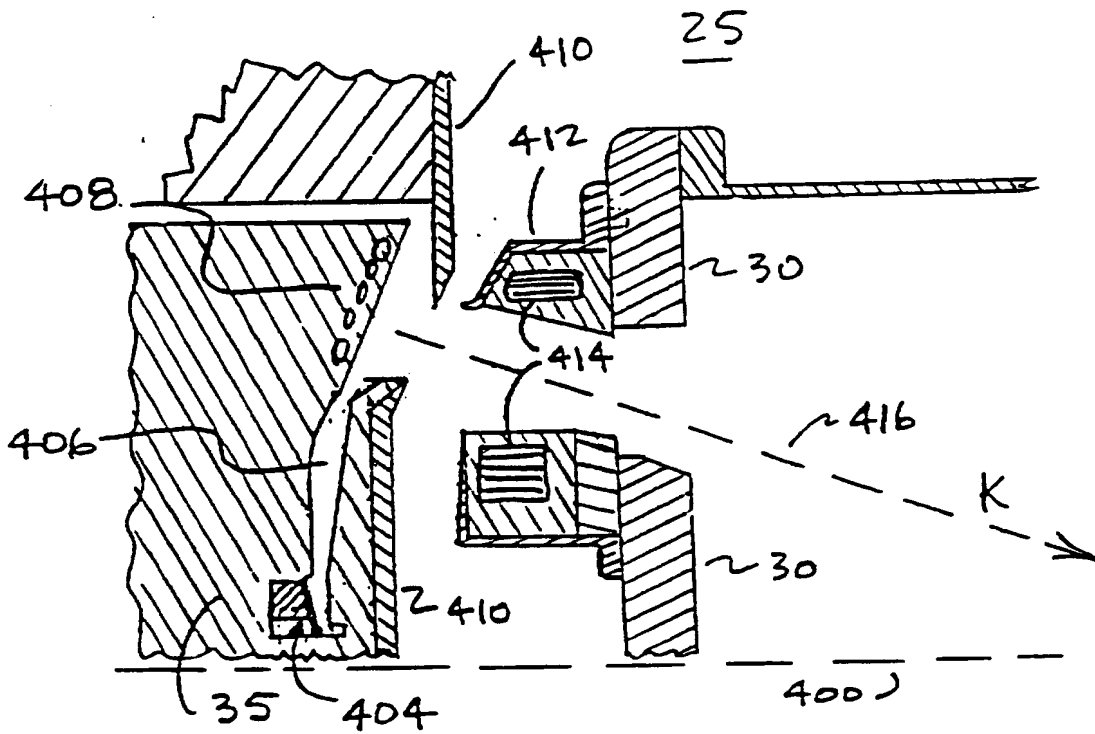


FIG. 2

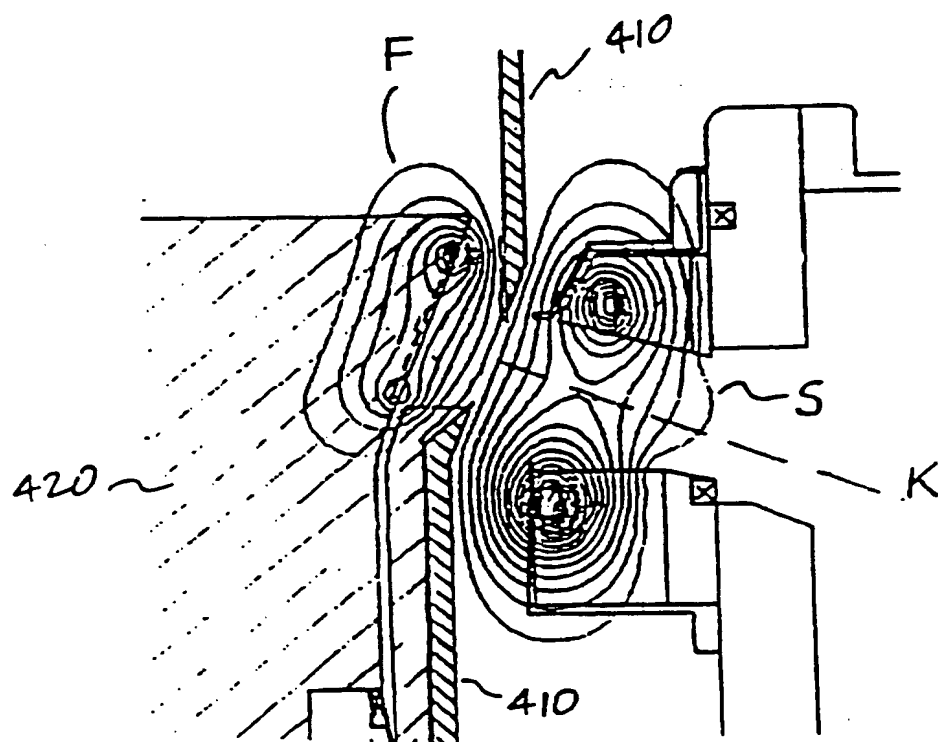


FIG. 2A

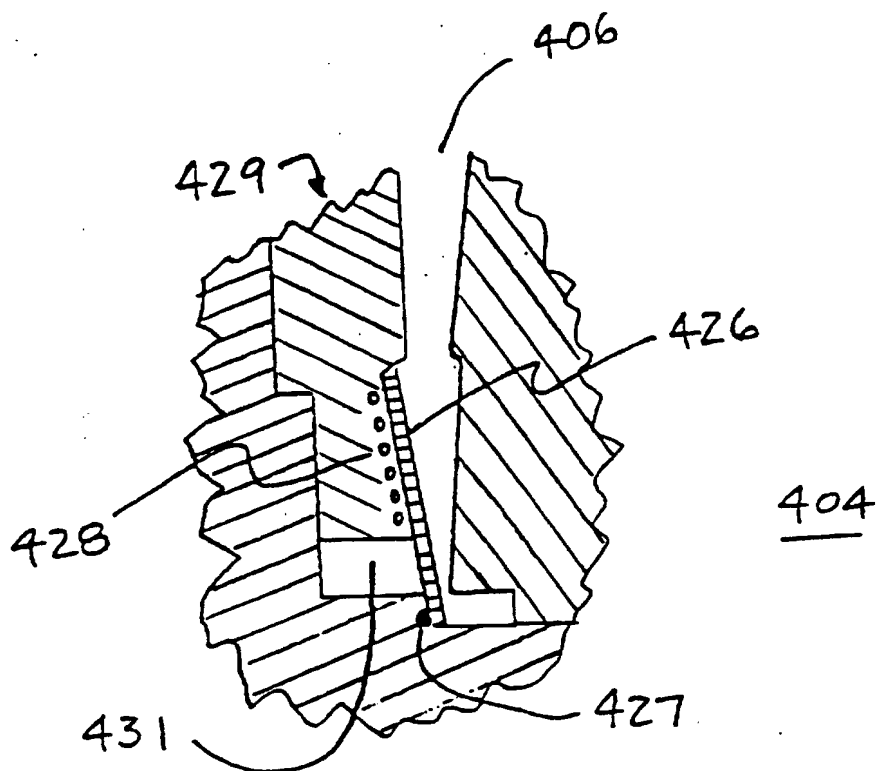


FIG. 2B

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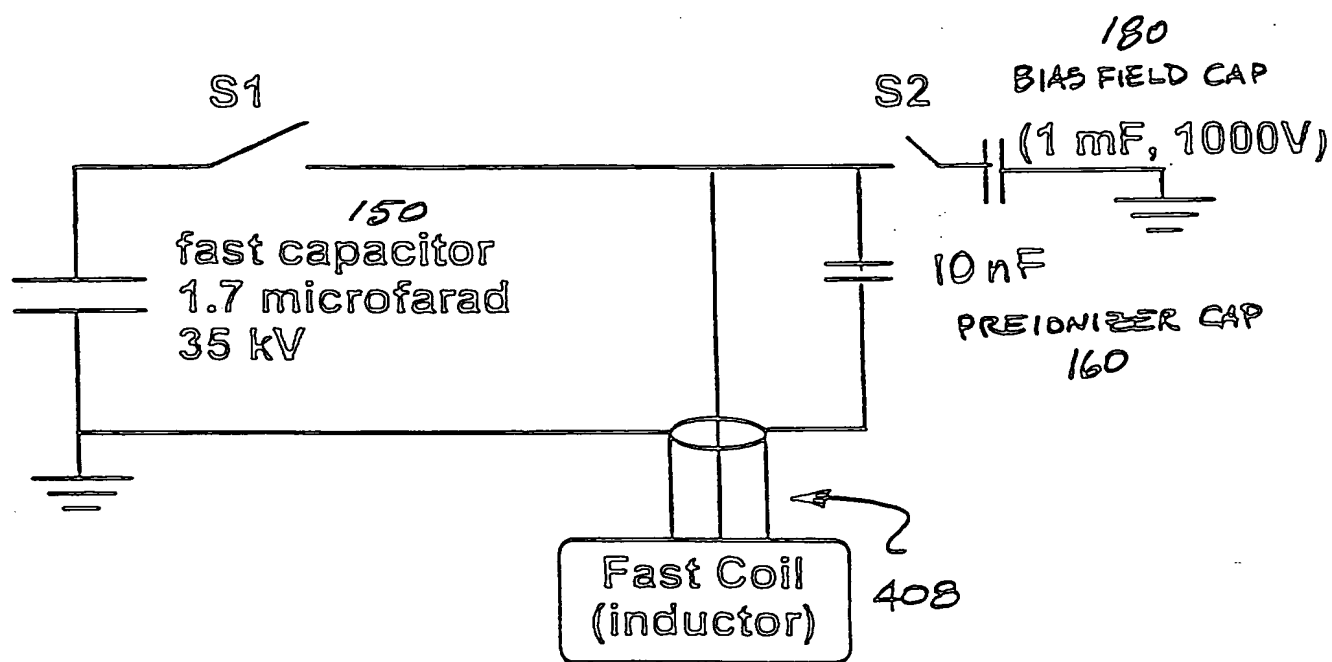


FIG. 2C

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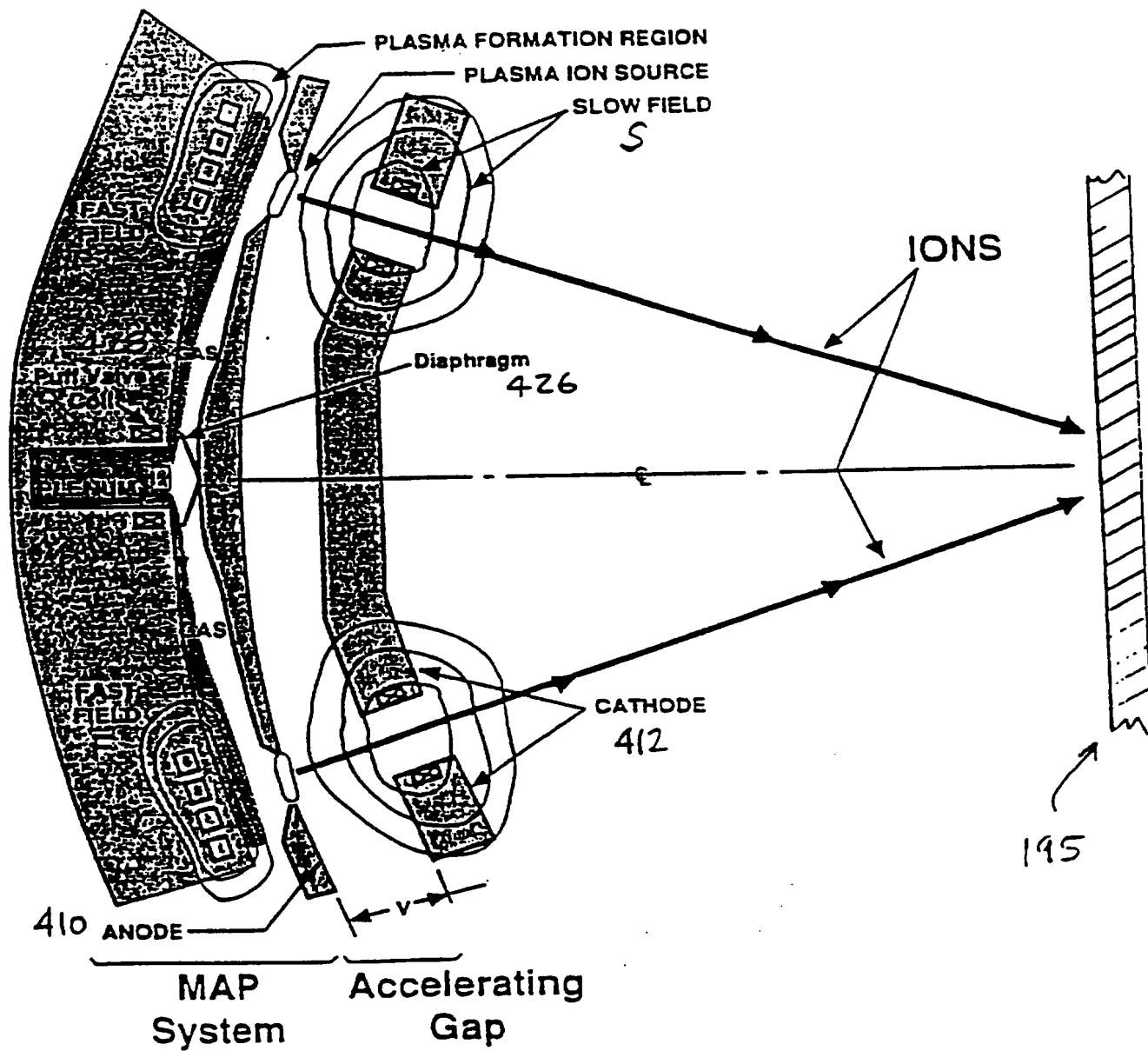


FIG. 3

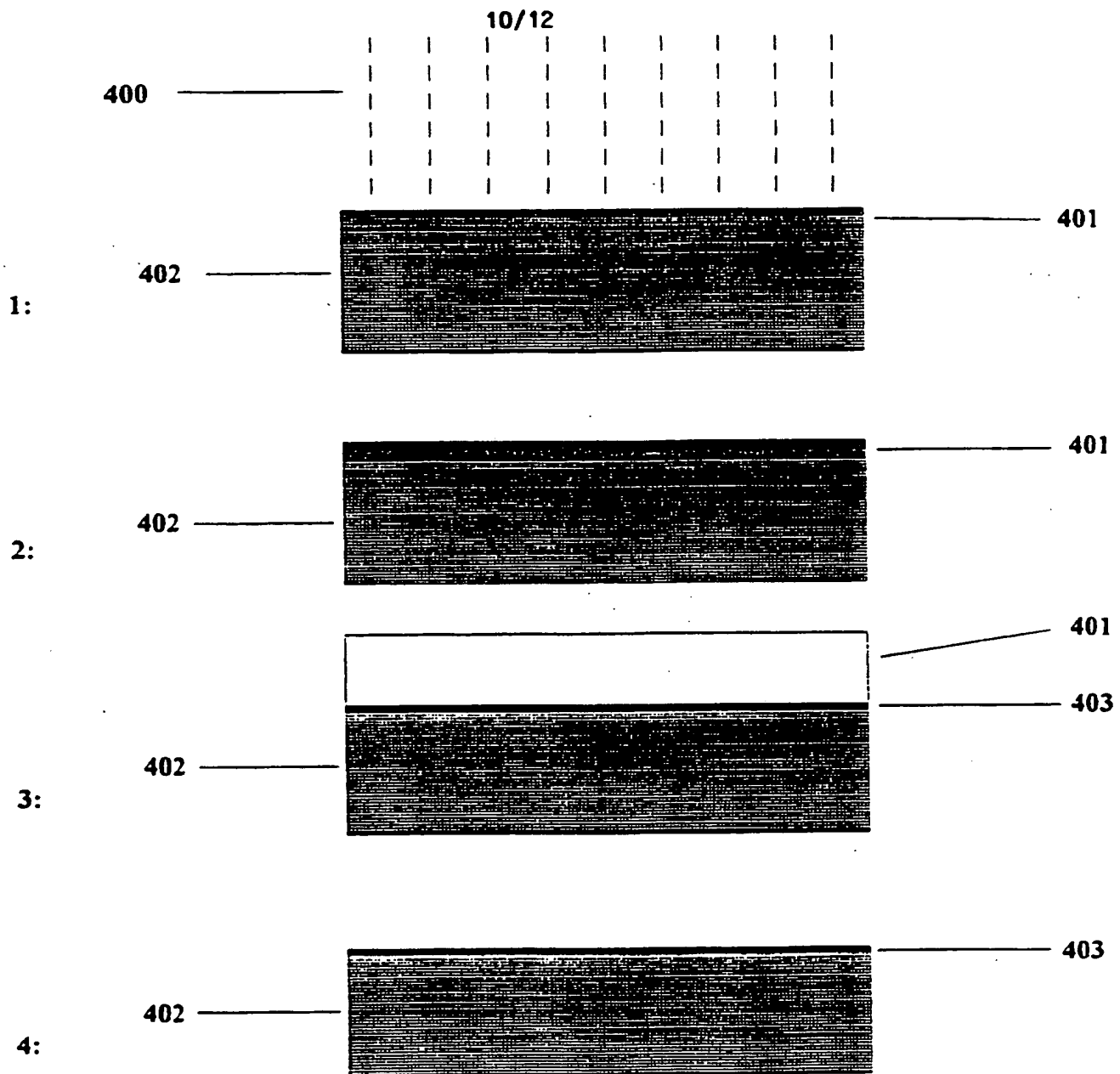


Figure 4A

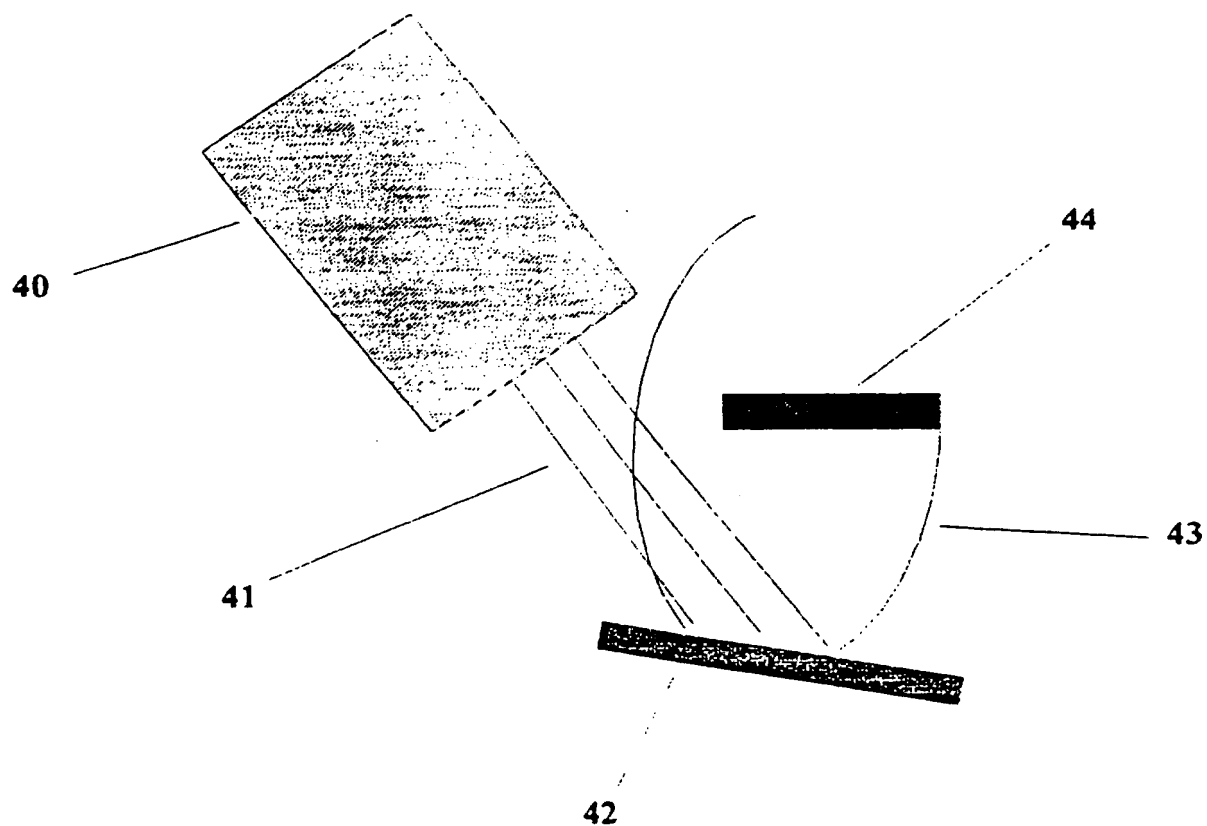


Figure 4B

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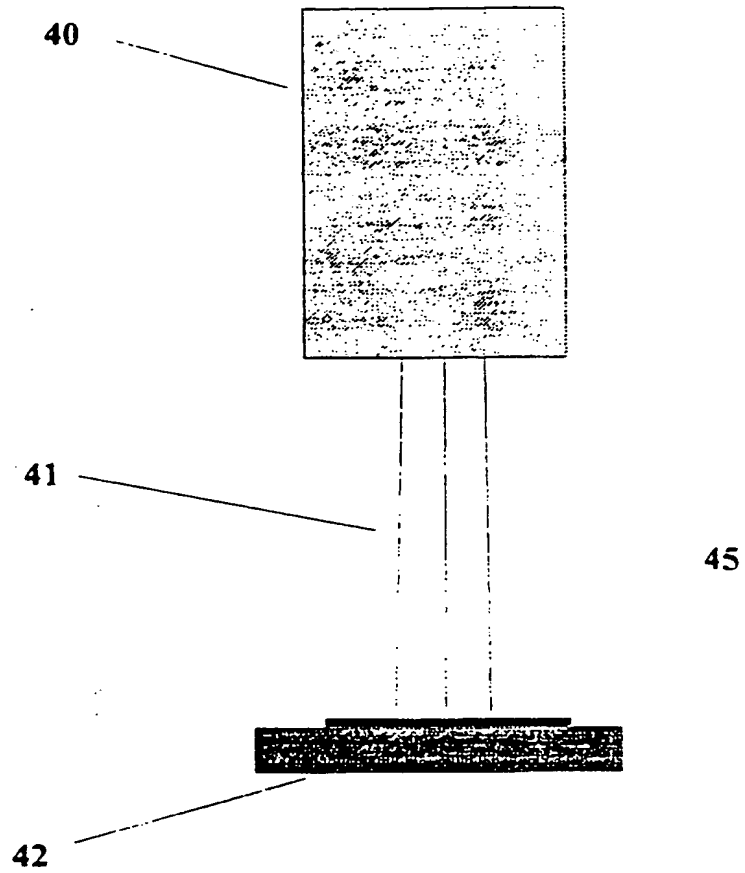


Figure 4C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/01000

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 118/696, 718, 723 FI; 427/140, 255.5, 272, 282, 492, 523,533,557,559,569,585

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 4,684,535 (Heinecke et al) 04 August 1987, entire document.	1-55
A	US,A, 4,727,234 (Oprysko et al) 23 February 1988, entire document.	1-55

☐ Further documents are listed in the continuation of Box C.

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Date of the actual completion of the international search

19 APRIL 1996

Date of mailing of the international search report

04 JUN 1996

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Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/01000

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

B05C 11/00; B05B 1/32, 3/02, 3/06; C08F 2/46; C23C 8/00, 14/00, 16/00; H05H 1/00, 1/24

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

118/696, 718, 723 FI; 427/140, 255.5, 272, 282, 492, 523, 533, 557, 559, 569, 585

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